Development of a vacuum membrane distillation unit operation: From experimental data to a simulation model

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Antonia Rom *, Walter Wukovits, Friedl Anton

Vienna University of Technology, Getreidemarkt 9/ E166, Vienna 1090, Austria

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A B S T R A C T

Due to the important role of thermal membrane separation processes for the chemical industry, simulation of those process steps is more and more relevant. In the simulation software AspenPlus© no unit operation for a membrane distillation step is available. Due to the lack of built in membrane distillation (MD) models, the aim of this work was to develop one for application in conceptual design on the AspenPlus© platform. Therefore, this paper presents a user-customize one dimensional unit operation for vacuum MD on the basis of the dusty gas model. Binary butanol water mixtures of different concentrations served as feed streams. Experimental investigations on a hollow fibre and tubular polypropylene (PP) membrane module with a pore diameter of 0.2 μm resulted in raw data on transmembrane flux and selectivity. These experiments served to generate a component permeance data bank. On the basis of the results, a regression for the component permeance was performed. The implementation of the generated permeance functions in the programming code resulted in a unit operation in AspenPlus© reproducing well the experimental work. Comparison of the model with the laboratory results show very good reliability for the different membranes investigated.

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1. Introduction

In the work of Lawson and Lloyd [1], membrane distillation (MD) was described as a relatively new process with several benefits compared to conventional separation steps like distillation and reverse osmosis. Fifteen years later, an increasing number of research papers show the important role of this thermal separation process. A variety of different MD types such as sweep gas MD, air gap MD, direct contact MD and vacuum MD offer several application possibilities like desalination, environmental/waste cleanup or food production [2–5].

In this paper the focus lies on vacuum membrane distillation (VMD) a relatively small investigated MD type [4]. VMD can be used as a separation step for volatile organic compounds from aqueous solutions. A possible use of this application is during continuous aceton–butanol–ethanol fermentation process to overcome product inhibition at low alcohol concentrations of

around 13 g/l [6]. Due to the high potential of the biobutanol market, optimization of the fermentation process by an in-situ separation of butanol from the fermentation broth is desired [7]. Besides pervaporation, gas stripping and liquid–liquid extraction [8–10], VMD is one of the separation processes investigated. In the work of Vane [10], VMD is outlined with many shortcomings like low selectivity compared to pervaporation. Still, VMD with condensation temperatures of 3 °C and moderate vacuum pressures of about 50 mbar has some energy-saving advantages. This special research field applied as separation of butanol from aqueous solutions is investigated in this paper.

VMD is a quite new commercially available process, but not yet on an industrial scale. Therefore, there is a lack of built in MD models in simulation engines like AspenPlus© up to now. However, simulation, as the key link between experimental work and industrial application, has to be given special consideration. Different researchers focused on the simulation of thermal membrane separation processes and the result is a variety of developed models [11–14]. In the work of Schiffmann and Repke [14], a rigorous pervaporation model was presented. Results showed that the discrete model itself already generates simulation data with sufficient accuracy. Also, Chang et al. [13] invented a membrane distillation model for desalination on the AspenPlus© platform, which is applicable for direct contact MD as well as air

Nomenclature

A   Membrane area (m^2)
J_i Transmembrane mass flux of component i ($kg/m^2 h$)
K_i Permeance of component i ($kmol/m^2 h\, bar$)
M_i Molar flux of component I ($kmol/h$)
m   Mass (kg)
n   Molar mass (kmol)
N_i Transmembrane molar flux of component i ($kmol/m^2 h$)
p^{sat} Saturation pressure (bar)
p   Pressure (bar)
Re   Reynolds number (–)
w%   Weight per cent (kg/kg)
x   Molar fraction in liquid phase (kmol/kmol)
y   Molar fraction in vapor phase (kmol/kmol)

Indices
Feed   Feed side of the membrane
i,j   Component i,j
n   Number of cell
Perm   Permeate side of the membrane
Ret   Retentate side of the membrane

Greek letters
Δp_i Partial pressure difference (bar)
ε Porosity of the membrane (–)
λ Mean free path of the gas molecules (–)
τ Tortuosity of the membrane (–)
γ Activity coefficient of component i (–)

gap MD. Guan et al. published a one dimensional user customize unit operation for direct contact MD and vacuum MD.

Despite the development of unit operations, an important point concerning process simulations is to ensure the correctness of the calculated physical properties in the simulation software behind. Researchers have to exercise caution when discussing simulation results. The most sophisticated unit operation calculates wrong results, if the chosen physical properties do not fit the process parameters. The challenge lies in choosing the correct thermodynamic model for the parameters to be investigated.

When calculating the driving force in VMD the activity coefficients of the investigated components are needed. To calculate activity coefficients of a butanol-water mixture in AspenProperties[©], the established NRTL model is often chosen. In general, the NRTL activity coefficient model has shown great applicability in calculating liquid–liquid or liquid–vapor phase equilibria. The work of Prausnitz and Renon [15], where the NRTL model was proposed in 1968, is one of the most cited papers [16] and made its mark in the thermal chemical engineering world. In AspenProperties[©], the NRTL model is defined by temperature-dependent binary parameters, which are calculated from experimental data. Several databases are available which differ in their experimental data sets. Still the results are assumed similar, when calculating activity coefficients. By changing the property databases and the underlying data, these binary parameters differ quite widely in AspenPlus[©]. Facing this problem during simulation, the authors propose new binary parameters for the investigated butanol-water mixture in this work. This new generated database was then used with the developed unit operation.

As can be seen, research is starting to focus on the investigation of membrane distillation models for simulation operations. In this paper the development of a user-defined counter current MD model based on lab scale experiments is presented. With the

simulation tool AspenCustomModeler[©] a user-defined discretised model was generated. The new unit operation can be used in conceptual design to implement in a flow sheet or to simulate and balance overall processes. Furthermore comparison with other separation processes can be done.

2. Theory VMD

In contrast to other membrane separation steps mass transport in MD contains phase change from liquid to vapor phase. The liquid feed side is in contact with the porous hydrophobic membrane. The membrane offers a contact surface in the pores where the evaporation step takes place. The evaporation follows the normal vapor–liquid equilibrium with the advantage of the membrane building a barrier between liquid and vapor phase. In VMD a vacuum is applied on the permeate side of the membrane. This applied vacuum as well as the temperature on the feed side provides the necessary driving force for the mass transport in VMD. The permeate is in vapor phase and the condensation takes place outside of the membrane module [2,12]. Depending on the process conditions and the pore size of the membrane, the mass transport can be described by Knudsen diffusion, Poiseuille flow, molecular diffusion or their combination, where molecular–molecular or molecular-pore contacts have to be considered [1,17]. Despite these mass transport mechanisms, the dusty gas model is used in VMD as a general model [1,17,18]. In the dusty gas model the transmembrane molar flux is proportional to the vapor pressure difference between feed and permeate side of the membrane. The transmembrane molar flux is connected with the partial pressure difference through the component permeance K_i, as can be seen in Eq. (1).

$$N_i = K_i \Delta p_i = K_i(x_i \gamma_i p_i^{sat} - y_i p_{Perm}) \qquad (1)$$

The permeance is a component specific membrane property which is a function of the process conditions and membrane characteristics. Some rigorous models of the mass transport phenomena are investigated in literature. In these models K_i is discussed in detail, including tortuosity, porosity, pore size, as well as the mean free path of the gas molecules [11–13,17–19]. Since many specific membrane characteristics are needed for those highly sophisticated models, too detailed modelling is sometimes not possible. Access to required membrane specifications can be difficult and is not always needed on the level of conceptual design. Therefore, in this work the dusty gas model was used to calculate mass transport phenomena only considering the permeance K_i. Measured transmembrane flux was used to calculate the component permeances as explained in the next steps.

Next to Eq. (1) the transmembrane mass flux can also be described as the mass flow through the membrane, divided by the membrane area and the experimental time as described in Eq. (2).

$$J_i = \frac{m_i}{A_t} \qquad (2)$$

After transforming the transmembrane mass flux to a molar basis, the combination of Eqs. (1) and (2) gives the following correlation for the component permeance:

$$K_i = \frac{N_i}{A_t \Delta p_i} \qquad (3)$$

From Eq. (3) the permeance can be calculated by means of the applied process conditions namely membrane area and partial pressure difference as well as measured transmembrane mass flux and experimental time. Different influences on the permeance can be considered, by performing an ordinary least square regression